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Impact of Wildfires on Ozone Exceptional Events in the Western U.S.

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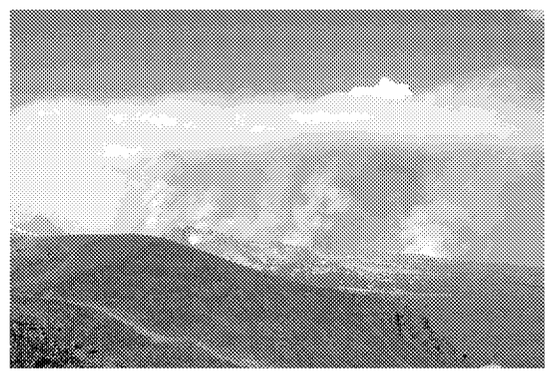
Supporting Information

ABSTRACT: Wildfires generate substantial emissions of nitrogen oxides (NO_x) and volatile organic compounds (VOCs). As such, wildfires contribute to elevated ozone (O_3) in the atmosphere. However, there is a large amount of variability in the emissions of O_3 precursors and the amount of O_3 produced between fires. There is also significant interannual variability as seen in median O_3, organic carbon and satellite derived carbon monoxide mixing ratios in the western U.S. To better understand O_3 produced from wildfires, we developed a statistical model that estimates the maximum daily 8 h average (MDA8) O_3 as a function of several meteorological and temporal variables for three urban areas in the western U.S.: Salt Lake City, UT; Boise, ID; and Reno, NV. The model is developed using data from June-September 2000−2012. For these three locations, the statistical model can explain 60, 52, and 27% of the variability in daily MDA8. The Statistical Model Residual (SMR) can give information on additional sources of O_3 that are not explained by the usual meteorological pattern. Several possible O_3 sources can explain high SMR values on any given day. We examine several cases with high SMR that are due to wildfire influence. The first case considered is for Reno in June 2008 when the MDA8 reached 82 ppbv. The wildfire influence for this episode is supported by PM concentrations, the known location of wildfires at the time and simulations with the Weather and Research Forecasting Model with Chemistry (WRF-Chem) which indicates transport to Reno from large fires burning in California. The contribution to the MDA8 in Reno from the California wildfires is estimated to be 26 ppbv, based on the SMR, and 60 ppbv, based on WRF-Chem. The WRF-Chem model also indicates an important role for peroxyacetyl nitrate (PAN) in producing O_3 during transport from the California wildfires. We hypothesize that enhancements in PAN due to wildfire emissions may lead to regional enhancements in O_3 during high fire years. The second case is for the Salt Lake City (SLC) region for August 2012. During this period the MDA8 reached 83 ppbv and the SMR suggests a wildfire contribution of 19 ppbv to the MDA8. The wildfire influence is supported by $PM_{2.5}$ data, the known location of wildfires at the time, HYSPLIT dispersion modeling that indicates transport from fires in Idaho, and results from the CMAQ model that confirm the fire impacts. Concentrations of $PM_{2.5}$ and O_3 are enhanced during this period, but overall there is a poor relationship between them, which is consistent with the complexities in the secondary production of O_3. A third case looks at high MDA8 in Boise, ID, during July 2012 and reaches similar conclusions. These results support the use of statistical modeling as a tool to quantify the influence from wildfires on urban O_3 concentrations.



I. INTRODUCTION

Wildfires generate substantial emissions of particulate matter (PM) and ozone (O_3) precursors.[1,2] They are also a major driver for interannual variations in summer air quality in the western U.S. for O_3,[3] PM[4] and black carbon aerosol.[5] However, O_3 production from wildfires is highly variable. In a recent review on O_3 production, the majority of published studies identified a positive relationship between carbon monoxide (CO) and O_3 in wildfire plumes, which is a good indicator of O_3 production.[6] For boreal and temperate fires, the $\Delta O_3/\Delta CO$ ratios were on average 0.018 ± 0.051, 0.15 ± 0.03 and 0.22 ± 0.23 ppbv ppbv^{-1} (±1 s.d.) for plumes aged 1−2 days, 2−5 days and ≥5 days, respectively, showing that O_3 production generally increased with age of the plume, but with large plume-to-plume variability.

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O_3 production is complicated by a number of factors including highly variable emissions,[1,7] aerosol effects;[8,9] complex meteorology and emissions of oxygenated VOCs[1,10,11] that can result in rapid conversion of NOx to PAN. If a wildfire plume mixes with urban emissions, more rapid O_3 production than either the fire or urban emissions would generate by themselves is likely.[12,13] The complexity of emissions, meteorology, radiation and aerosol effects make it very difficult to accurately model O_3 photochemistry using standard Eulerian chemical models.

For O_3, the U.S. EPA uses the 1 h daily maximum and the maximum daily 8 h average O_3 (MDA8) for its regulatory standards. Across most of the western U.S., background O_3 is already elevated due to the high elevations and exposure to the free troposphere.[14−17] During high fire years the distribution of MDA8 values across the western U.S. shifts by 5−7 ppbv, making compliance with the O_3 standard much more challenging.[14] For this reason, the EPA has developed a policy on "exceptional events," which can be defined as "Unusual or natural events that affect air quality but are not reasonably controlled..." (see http://www.epa.gov/ttn/analysis/exevents.htm). Exceptional events can include natural dust storms, transport from sources outside of North America, transport of air from the upper troposphere or lower stratosphere or pollution impacts due to wildfires. To exclude data from consideration, a region must submit a request to EPA that demonstrates, quantitatively, that the air quality would have met the appropriate standard but for the exceptional event.

One approach to identify exceptional events is to use a regression model that calculates O_3 mixing ratios as a function of various meteorological variables. In most cases, daily maximum temperature has been found to be the best predictor for peak or MDA8 O_3 at most sites.[18] Other studies have included a wide array of meteorological variables, such as temperature, cloud cover, or humidity to improve the model fit.[19,20] In one study of 74 regions in the eastern U.S.,[21] 10 different variables were considered in the model. Daily maximum temperature and daily average relative humidity (RH) were found to be the most important predictors for MDA8 O_3. Using a generalized additive model, the authors were able to predict the MDA8 values with an R^2 of 0.5−0.7 for most sites.

In this paper we demonstrate a statistical model that can predict the MDA8 O_3 for three metropolitan regions in the western U.S.: Salt Lake City, Utah; Boise, Idaho; and Reno, Nevada. For three cases we examine days that have high residuals from the statistical model and propose that these were due to wildfire influence based on a variety of supporting data (e.g., Community Multiscale Air Quality (CMAQ) and Weather Research and Forecasting Model with Chemistry (WRF-CHEM) Eulerian models, satellite data, air mass trajectories, etc). The residual from this statistical model can provide quantitative information on the O_3 contribution. This work can help guide future analyses to quantify the influence of wildfires on O_3 in urban areas, in support of exceptional event designations.

II. MATERIALS AND METHODS

We used data from a variety of sources for this analysis including the EPA's AQS sites, CASTNET O_3 measurements, NPS O_3 measurements, IMPROVE aerosol measurements, meteorological data from NCDC and satellite observations from instruments onboard the NASA A-train constellation. Gridded meteorological data were from the NCEP/NCAR Reanalysis data set. For the Salt Lake City (SLC) urban area, we used the daily average MDA8 from all AQS sites in Salt Lake and Davis Counties, Utah (up to four sites). For Boise and Reno, we used the daily average of all MDA8 values in each metropolitan statistical area as defined by EPA (up to three and six sites, respectively). We also used surface meteorological data from the SLC, Boise and Reno airports. We used satellite data for CO mixing ratios derived for 800 mb from the AIRS instrument onboard the Aqua satellite and aerosol optical depth (AOD) from the MODIS instruments on board the Aqua and Terra satellites. When daily data from both instruments were available, we averaged the AOD values. For all analyses, we used data for the primary fire season, June−September 2000−2012, except there is no data for Boise in 2000. Further details and data sources are given in Table S1 in the Supporting Information.

We used two different Eulerian models to help quantify the contribution to the MDA8 from wildfires, since neither model had results for the full time period of our study. For the 2012 wildfires, we used the CMAQ model[22] to quantify the influence of wildfires on O_3 concentrations. CMAQ is a peer-reviewed, state-of-the-science Eulerian photochemical model that is run daily as part of the experimental BlueSky Gateway air quality modeling system, which quantifies air pollutant concentrations resulting from wildfires and other emissions sources on a national scale.[23] BlueSky Gateway combines meteorological predictions from the Pennsylvania State University/National Center for Atmospheric Research Mesoscale Model (MM5) version 3.7 with air quality predictions from CMAQ version 4.5.1 at a coarse (36 km) grid resolution, and aerosol tracers have been implemented in CMAQ to track primary $PM_{2.5}$ generated by fires. Fire emissions in the CMAQ simulations were derived from fire activity data (locations and acres burned) and the SMARTFIRE system. Fuel loadings were derived from the Fuel Characteristic Classification System (FCCS), fuel consumption is estimated by the Consume 3.0 model, and fire emissions are calculated using the Fire Emission Production Simulator (FEPS). The emissions for each fire event vary by day and hour as the fire progresses. For the summer of 2012, CMAQ was run with and without fire emissions to evaluate fire impacts on O_3 concentrations across the U.S.

For 2008, we performed simulations with the regional WRF-Chem version 3.2[24] to quantify the influence from wildfires. The model covers the contiguous U.S. at a horizontal resolution of 24 × 24 km and is run for the time period from 10 June to 10 July 2008. The anthropogenic emissions are obtained from the U.S. EPA 2005 National Emissions Inventory (NEI-2005). Biomass burning emissions are obtained from the Fire INventory from NCAR (FINN V1)[25] and are distributed in the model vertically following the online plume-rise module.[26] The model is configured for the MOZART gas phase chemical scheme linked to the GOCART aerosol model.[27] A more detailed description of the model configuration can be found in ref 28.

In addition to standard chemical tracers we include in these model runs a synthetic tracer that keeps track of O_3 that is due to NO_x emissions from fires. The O_3 tracer method or "XNO_x" method is described in detail in ref 29 and has been used in global models for identifying source contributions, such as for quantifying the O_3 budget[30−34] and here for the first time it has been applied in a regional model. The method tags emissions of

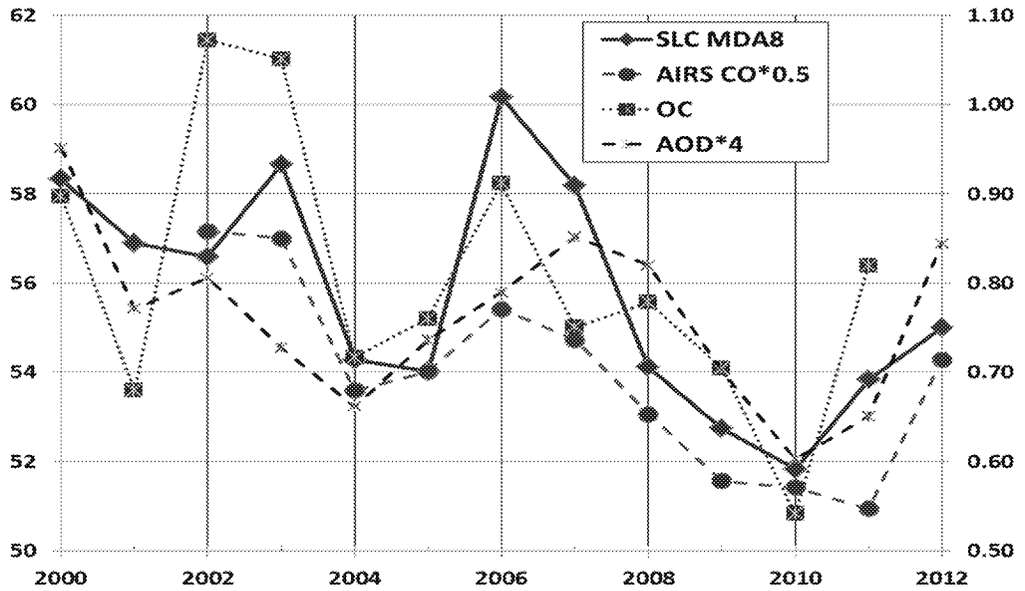

Figure 1. Time series of summer (June–September) median MDA8 (ppbv, left axis) from Salt Lake City urban area. Also shown are summer median organic carbon (OC, $\mu g/m^3$, right axis) from three background IMPROVE sites (CRM, PND, GRB) and two satellite observations: CO and AOD. Units are ppbv (left axis) for SLC MDA8, ppbv*0.5 (left axis) for the AIRS CO data, $\mu g\ m^{-3}$ (right axis) for OC. For AOD, the value is multiplied by 4 and shown on the right axis. The correlation coefficient between the annual median SLC MDA8 and OC, AIRS CO and AOD are 0.75, 0.86, and 0.58, respectively. For satellite data (CO and AOD), these are averaged over 38–43° N −110–115° W.

Table 1. Regression Models for SLC, Boise and Reno MDA8 (ppbv)[a]

	unstandardized coefficients		standardized coefficients		
SLC model	B	std. error	beta	t	sig.
constant	814	95.8		8.50	0.000
daily max temp	1.29	0.035	0.634	36.7	0.000
daily avg. wind spd.	−0.197	0.014	−0.237	−13.7	0.000
yr	−0.388	0.048	−0.132	−8.14	0.000
DOY^2	-1.95×10^{-4}	1.24×10^{-5}	−0.256	−15.6	0.000
700 mb zonal wind	−0.615	0.076	−0.140	−8.06	0.000
	unstandardized coefficients		standardized coefficients		
Boise model	B	std. error	beta	t	sig.
constant	781	111		7.03	0.000
daily max temp	1.02	0.036	0.562	28.1	0.000
daily avg. wind spd.	−0.087	0.019	−0.087	−4.59	0.000
yr	−0.372	0.055	−0.123	−6.74	0.000
DOY^2	-1.85×10^{-4}	1.34×10^{-5}	−0.260	−13.8	0.000
700 mb zonal wind	−0.521	0.068	−0.151	−7.66	0.000
	unstandardized coefficients		standardized coefficients		
Reno model	B	std. error	beta	t	sig.
constant	32.6	1.49		21.9	0.000
daily max temp	0.813	0.039	0.456	20.7	0.000
DOY^2	-1.11×10^{-4}	1.27×10^{-5}	−0.193	−8.76	0.000
700 mb zonal wind	−0.189	0.059	0.071	−3.20	0.001

[a]Overall R^2 for the SLC, Boise and Reno models are 0.60, 0.52, and 0.27, respectively. Units for MDA8, T_{max}, and wind speeds are ppbv, °C and m sec^{-1}, respectively. Inclusion of previous day's MDA8 increases the R^2 values to 0.65, 0.57, and 0.47, respectively. Note that while DOY is initially included as a quadratic term, there is no difference in the final model fit by including it as a squared term.

NO and its resulting nitrogen-containing products (e.g., HNO_3, PAN, HNO_4, etc.) and follows them to the production of O_3. In addition to the standard tagging method, we further conducted a simulation where we did not allow O_3 to be produced through PAN decomposition from fires, in order to provide an estimate of the role of PAN on O_3 production in fire plumes.

III. RESULTS

As noted above, there are large interannual variations in the summer mean MDA8, with a range of 49–58 ppbv for SLC. To examine the relationship between seasonal MDA8 and other parameters that are likely associated with wildfires, we compared the SLC and regional MDA8 with organic carbon, AIRS CO and AOD. Figure 1 shows this comparison using

summer median values for 2000–2012. In all cases, the median values are significantly correlated ($p \leq 0.05$) with SLC median MDA8. Thus it is reasonable to propose that wildfires in the western U.S. may be the primary driver to explain these large interannual variations and may cause a significant shift in median MDA8, up to +9 ppbv in SLC. While this broad seasonal comparison does not help identify wildfire impacts on individual days, it does demonstrate the challenge regions have in meeting the O_3 air quality standard during high fire years. Also apparent in Figure 1 is a downward trend in median MDA8 values in the SLC region. This is likely due to regional emissions controls, as demonstrated by the downward trend in urban NO_x concentrations for the SLC region. NO_x concentrations in the region have decreased approximately 5% per year since 2000 (see http://www.epa.gov/airtrends/nitrogen.html).

Statistical Model Development. We used PASW Statistics software (now IBM SPSS Statistics) version 18.0.3, to develop the statistical model. For each location, we examined the multilinear relationship (MLR) between the indicated variable and the regional averaged daily MDA8 value for June–September. A large number of variables were considered to identify the best model including surface variables (daily maximum temperature, daily average wind speed) and upper air parameters (see Table S1). We identified the variables that gave the strongest explanatory power (correlation) with the least multicollinearity, as this would confuse the interpretation of the model results.[35] For all locations, we found that daily maximum temperature was the strongest predictor for MDA8. Supporting Information Figure S1 shows a scatter plot of MDA8 versus daily maximum temperature for SLC. However, other variables also show a significant relationship with MDA8 and should be included in the model. The MLR model fits an equation of the form

$$\text{MDA8} = a + bX_1 + cX_2 \ldots + \text{residual}$$

Where the MDA8 is the dependent variable, X_1, X_2, etc. are the independent predictors, a, b, c, etc. are the coefficients and the residual is the unfit portion of the model. In this analysis we refer to the residual as the statistical model residual (SMR). We examined the best form for each predictor including linear, squared, quadratic, log, etc. For most variables a linear fit gave the best performance, except for day of year, where a squared term yielded an improved fit.

We also examined the performance of generalized linear models (GLM) as a tool to build the statistical models, but did not find a significant improvement in predictive ability. Therefore we used the simpler MLR approach, which makes interpretation of the predictors more straightforward.

Table 1 summarizes the model predictors and Table 2 provides a summary of the daily MDA8 and daily model residuals for each location. For SLC and Boise, the best fit model explained 60 and 52% of the variance in MDA8 values. For these two regions we found that daily maximum temperature, daily average surface wind speed, day of year^2, year and the 700 mb zonal wind component gave the best fit with minimal multicollinearity. Inclusion of additional meteorological variables made virtually no difference to the model fit. Expanding the analysis to include May data generally reduced the performance of the model in all three locations. For Reno, the model explained less of the total variance (27%) and the variables included only daily maximum temperature, day of year^2 and the 700 mb zonal wind component. The most likely explanation for this is that SLC and Boise, are more isolated cities, whereas Reno is adjacent to larger emissions sources in California. We expect that a parameter that included a better measure of transport from California might explain more of the variance in MDA8 values.

Table 2. Statistical Summary of SLC, Boise, and Reno MDA8 and Model Residuals (June–September)

	N	minimum	maximum	mean	std. deviation
SLC MDA8	1585	19.7	101.5	55.8	11.0
SLC Resid.	1582	−24.7	34.3	0.0	7.0
Boise MDA8	1449	17.0	86.0	50.9	10.3
Boise Resid.	1449	−30.8	26.1	0.0	7.2
Reno MDA8	1586	24.8	82.0	52.8	8.4
Reno Resid.	1586	−27.7	25.9	0.0	7.2

Because the MDA8 values have significant autocorrelation, inclusion of the previous day's MDA8 value will improve the model fit. For SLC and Boise, this improvement was relatively minor (R^2 values increased by 0.05 for each), whereas for Reno the model fit was improved substantially (R^2 increased by 0.20). For most days, this had relatively little impact on the calculated residual, except in a multiday pollution event. For such an event, the residual for the second and succeeding days was reduced if the previous day's MDA8 was included as a model predictor. However, since our goal is to identify exceptional events, we feel that these should be predicted from meteorological parameters alone, not the previous day's MDA8 values. Thus the final statistical model used in this analysis does not include the previous day's MDA8 as a predictor. As a result, the SMRs show significant autocorrelation. We examined the influence that this autocorrelation has on the SLC model results as follows. We removed 80% of the data points by selecting data on only every fifth day and then reran the model with the same predictors. We found that this made very little difference in the overall R^2 of the model and all predictor variables remained statistically significant. The residuals from this reduced data model (every fifth day) no longer show significant autocorrelation. With the reduced data set, the Durbin-Watson test confirmed no autocorrelation at a significance level of $p = 0.05$ (test statistic = 1.93), demonstrating that autocorrelation has minimal influence in the reduced data model. So, while autocorrelation is present in the residuals for the full data model, we found it has little influence on the predictors or the form of the model.

It is important to check the distribution of the residuals and the relationship with respect to the original independent variables. A histogram of the SMR values for SLC is shown in Supporting Information Figure S2 and a plot of SMR versus daily maximum temperature is shown in Supporting Information Figure S3. Mean and standard deviation (SD) for the SMRs for each location is shown in Table 2. At all locations, the SMR has a mean of 0 and a SD that is smaller than the SD of the MDA8. The residuals are normally distributed and show no pattern with respect to temperature. Similar results are found when the residuals are plotted against the other independent variables in the model for all locations.

Interpretation of the Statistical Model Residual (SMR). The SMR can yield information about days that have higher MDA8 than predicted from the input meteorological conditions. These days are then candidates to consider as exceptional events, but further evidence is needed to identify

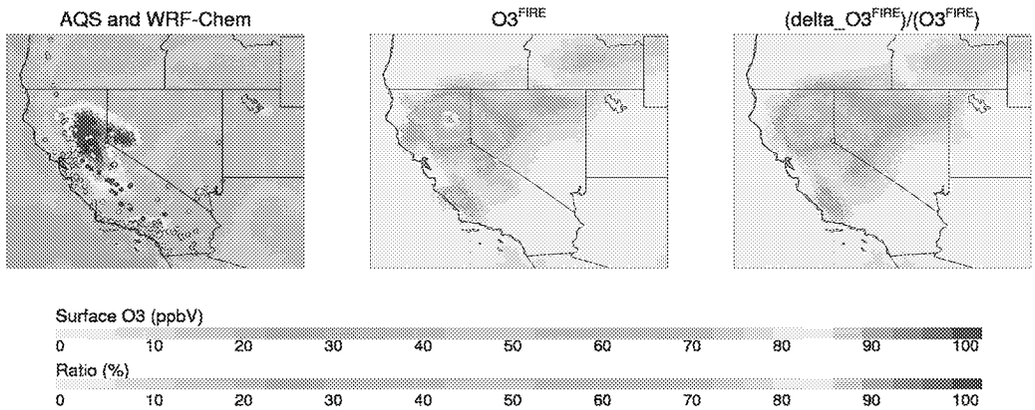

Figure 2. Surface O_3 from AQS sites for 24 June 2008 (circles) and WRF-Chem model results (ppbv, left panel), O_3 due to fires in WRF-Chem (ppbv, middle panel) and % of O_3 from fires where the NO_x cycled through PAN decomposition (%, right panel). Observations are an average for hours 15−17 local time, model results for 0 UTC (~16 local time).

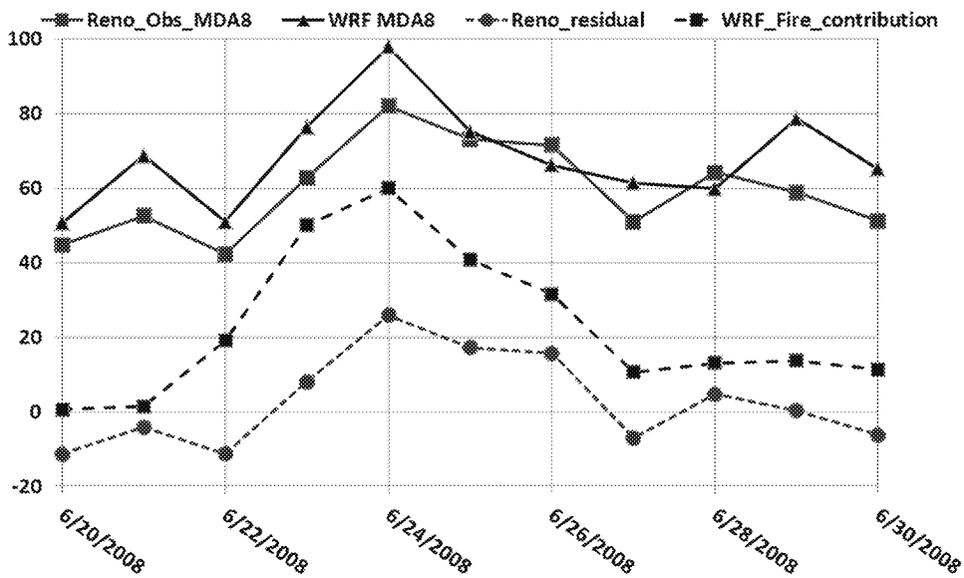

Figure 3. Observed MDA8 and residual from the statistical model for Reno. Calculated MDA8 from the WRF model and the model calculated contribution from fires.

the cause of high O_3. Possible causes for high SMR might include

(1) Additional precursors from unusual sources within the region;
(2) Additional O_3 produced from precursors emitted by wildfires;
(3) Unusually large contribution of O_3 from the upper troposphere/lower stratosphere (UTLS);
(4) Unusually large contribution from transport of O_3 and/or precursors from distant sources.

Both transport from Asian sources and transport from the UTLS have been previously identified as important sources of O_3 in the western U.S.[14,15,36−38] Wildfires have also been suggested as important O_3 sources,[6] especially in the western U.S.[3,6,34] To examine the utility of the SMR as a tool to quantify the influence on specific days, we will focus here on three cases with high SMR.

While 2008 was not an exceptional year over the entire western U.S., wildfires in California burned approximately 1.5 million acres in 2008 compared with 0.7 million acres on average for the state between 1997 and 2012 (data from the National Interagency Fire Center www.nifc.gov). Exceedances of the hourly O_3 standard were reported at a number of sites in California and several of these were considered "exceptional events" by the state.[39] Figure 2 shows the modeled O_3 for local afternoon on 24 June 2008. While the fires were located mainly in California, westerly winds carried plumes into Nevada, with O_3 reaching up to ~100 ppbv. A tagged WRF-CHEM model run indicates that between 40 and 60 ppbv of O_3 was contributed by the wildfires across a large section of western Nevada. Figure 3 shows a time series of the measured MDA8 and modeled MDA8 in Reno, NV, for 20−30 June 2008. The figure also shows the WRF-CHEM fire contribution to the MDA8 and the SMR. Both the measured and modeled MDA8 values peak on 24 June, as does the wildfire contribution and the SMR. The MDA8 in Reno on 24 June was 80 ppbv and the SMR suggests that 24 ppbv was due to the wildfire contribution. The calculated fire contribution using WRF-CHEM is 60 ppbv, a much higher value than the SMR; however, we expect this to differ as it shows the tagged contribution under the chemical regime of the fire plume, whereas the SMR is the residual from what is typical for the

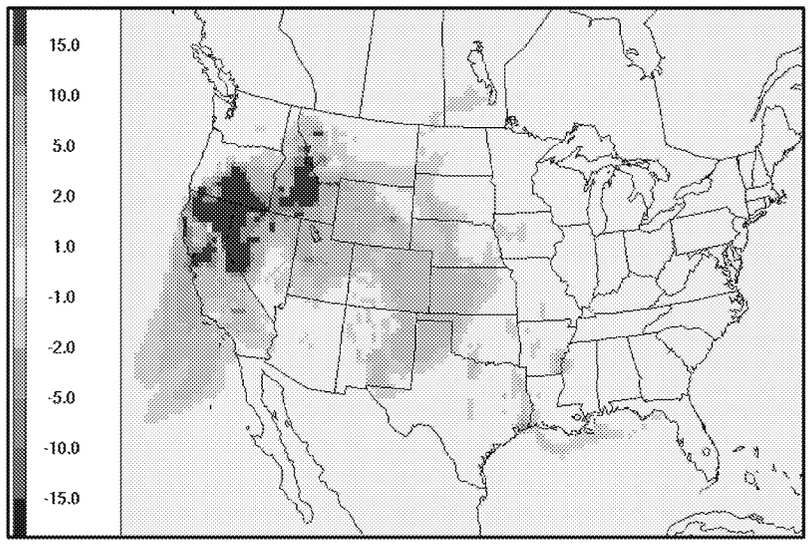

Figure 4. Calculated contribution to MDA8 (ppbv) on 12 August 2012 due to wildfires in the western U.S. This estimate is produced by running CMAQ with and without wildfire emissions. The difference is assumed to be the wildfire contribution. For SLC, the observed MDA8 is 80 ppbv. The modeled MDA8 is 74 ppbv, with a wildfire contribution of 5.5 ppbv. By comparison, the SMR for this day is 19.6 ppbv.

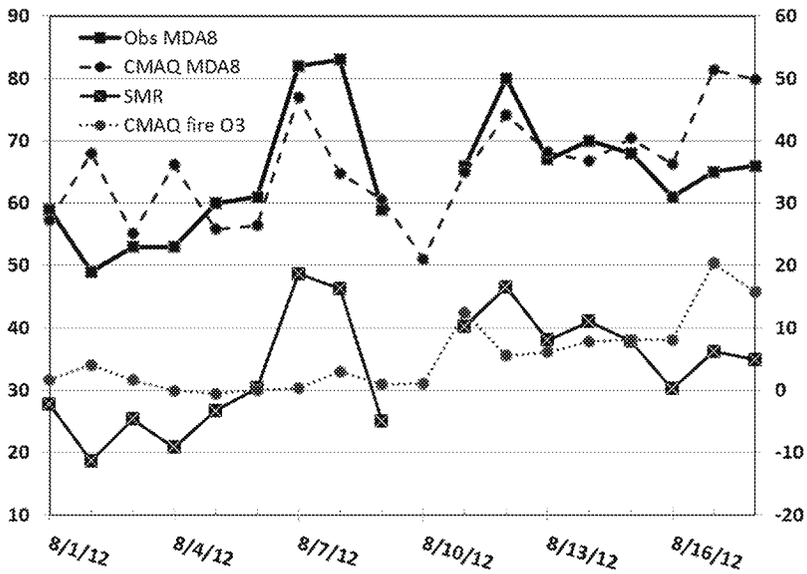

Figure 5. Observed and modeled (CMAQ) MDA8 for SLC for 1−18 August 2012 (left axis, ppbv). Also shown is the contribution due to wildfires from the CMAQ model and the SMR (right axis, ppbv). Observations and the SMR are not available for August 10, 2012.

meteorological conditions. The consistency in timing between the WRF-CHEM and observed values and the WRF-CHEM wildfire contribution supports the use of the SMR as an indicator of the magnitude of the wildfire contribution. The wildfire influence on 24 June is also supported by Supporting Information Figure S6, which shows the location of fires burning at the time, smoke from the MODIS instrument on the Aqua satellite and information on transport from HYSPLIT trajectories.

Figure 2 (right panel) also shows that a large fraction of the O_3 that is produced from wildfire precursors is due to NO_x that has been cycled through peroxyacetyl nitrate (PAN). Substantial production of PAN in wildfires has been noted previously,[10] and the WRF-CHEM results demonstrate the importance of PAN in generating O_3 far downwind of the fire region. This may also explain part of the reason O_3 and PM enhancements from some wildfires show little relationship[13] and suggests that fire influences on O_3 can occur far downwind of the emission source, driven by PAN transport and decomposition back to NO_x.

The 2012 wildfire season was unusually strong across most of the western U.S. In total more than 7 million acres burned in the western U.S. compared to approximately 4 million acres in an average year. Unusually large areas burned in California, Oregon, Idaho, Nevada and Montana in 2012. In late July and early August a large number of fires burned across northern California, southeastern Oregon, northern Nevada and southern Idaho. Figure 4 shows the contribution to the MDA8 due to wildfires for 12 August 2012 as calculated by the CMAQ model. Figure 5 shows the observed and CMAQ-modeled MDA8 for 1−17 August 2012, as well as the CMAQ fire contribution and the SMR. Over the period between 7 and 18 August, the average CMAQ wildfire contribution of 8 ppbv is very close to the average SMR of 9 ppbv. However, the CMAQ

model tends to underpredict peak MDA8 values in excess of 75 ppbv observed on 7, 8, and 12 August. The CMAQ model also shows a relatively weak correlation between the observed and modeled MDA8 for this period (R^2 = 0.21). On these days, the CMAQ modeled wildfire contribution are also lower than the SMR values. Supporting Information Figure S4 shows the relationship between observed MDA8 and daily average $PM_{2.5}$ for the SLC region during the fire influenced period. For this period, the R^2 for this relationship is 0.17, whereas in the CMAQ model it is 0.51. Thus we conclude that while the CMAQ model does capture some of the influence from the wildfires during this period, it has difficultly in accurately modeling the observed MDA8. Further evidence for a wildfire influence in SLC on 7 and 8 August is shown in Supporting Information Figures S7 and S8. These figures show the location of fires and smoke (from the NOAA Hazard Mapping System) and demonstrate that the smoke was clearly present in/around SLC on these dates.

For Boise, Idaho, results from the statistical model are shown in Tables 1 and 2. Supporting Information Figure S5 shows the SMR and CMAQ fire contribution for Boise in July 2012. During this time period, large fires burning in northern California, Oregon and Idaho were influencing air quality across the western states. The MDA8 values in Boise peaked at 74 ppbv on 11 July 2012. During this time period the CMAQ results showed a relatively weak correlation with the observed MDA8 values in Boise (R^2 of 0.12) and the calculated fire contributions were much smaller than the SMR values (see Supporting Information Figure S5). Further evidence for a wildfire influence in Boise on 11 July is shown in Supporting Information Figure S9. This figure shows the location of fires and smoke (from the NOAA Hazard Mapping System) and demonstrates that the smoke was clearly present in/around Boise on this date.

These findings highlight sources of error associated with the BlueSky Gateway CMAQ modeling, which include parametrizations used to solve the atmospheric momentum equations, spatial grid cell resolution, and uncertainties associated with fire emissions estimates.[23] As in the Reno case, the timing and magnitude of the observations and the Eulerian model results support the use of the SMR to quantitatively characterize the O_3 production due to wildfires.

IV. DISCUSSION AND SUMMARY

Figure 1 demonstrates that wildfires can have a significant influence on MDA8 levels in urban areas of the western U.S., but quantifying the daily impact is a challenge. Development of a statistical model for O_3 is an important and useful exercise that can indicate the types of meteorological conditions that are conducive to O_3 formation in a specific region. Outliers from this model, called the SMR, can then indicate unusual sources of O_3 or unusual conditions that may qualify as exceptional events per the EPA definitions. For cases where corroborating analyses point to the influence of fire emissions on elevated O_3 concentrations, the SMR can provide an estimate of this impact. This may then satisfy EPA's requirement of a quantitative demonstration that O_3 levels would not have exceeded the standard "but for the unusual" event. The statistical modeling technique described in this paper is able to provide this estimate without requiring the resources and expertise needed for complex Eulerian photochemical modeling of wildfire impacts.

We have estimated the magnitude of the wildfire impact on MDA8 for three cases using the SMR and two different Eulerian models (WRF-Chem and CMAQ). None of these calculations can be considered exact, nor can they be considered identical. Each method gives an estimate of the true wildfire contribution for the given case. The SMR value likely underestimates the true impact. This is because the value is calculated as the outlier, and thus ignores any background or average wildfire contribution that is embedded in the seasonal cycle or relationship with temperature. For the CMAQ calculation, the wildfire contribution is calculated as the difference in model runs with all wildfires emissions turned on/off. Using WRF-Chem, the contribution is calculated by tagging each emission source and using this to quantify the O_3 production. The WRF-Chem results also demonstrate an important role for PAN in redistributing primary wildfire emissions and enhancing O_3 over a larger region. One consequence of PAN chemistry and complex aerosol effects is that O_3 and aerosol enhancements associated with wildfires show minimal correlation.

■ ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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